Relation of Antiknock Value of Gasoline to Its Volatility and Solubility in Liquid SO_2

A Dissertation Submitted in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy in the University of Michigan

by

HENRY TIBBELS WARD

Reprinted from The Oil and Gas Journal, issue of June 1, 1933

*D 1454

R. UNIV.
BIBLIOTHEEK
LEIDEN

Relation of Antiknock Value of Gasoline to Its Volatility and Solubility in Liquid SO_2

By HENRY T. WARD* and ALFRED H. WHITE

In recent years the knock ratings have been determined for a considerable number of the individual hydrocarbons which occur in gasoline; there is also available in the literature some information as to the solubility of various hydrocarbons in liquid sulphur dioxide. From a study of the published data in these two lines one would conclude that there should be at least a trend in the relation between the knock ratings of gasolines and their solubility in liquid sulphur dioxide at some chosen temperature, particularly if gasolines of approximately the same volatility were selected.

It was not to be expected that an exact quantitative relationship could be developed, since, in general, knocking characteristics of hydrocarbons in homologous series are much more affected by slight differences in structure than are the solubilities in a given solvent. For instance, heptane and iso-octane are both relatively insoluble in liquid sulphur dioxide, although they differ by 100 octane numbers in knock rating.

The present paper records observations on the knock ratings and sulphur dioxide solubilities of certain specially prepared naphthas and of 29 commercial gasolines, and shows that for fuels of approximately the same volatility, there is a distinct trend toward higher knock ratings as the solubility in sulphur dioxide increases.

Apparatus for Extraction With SO_2

Although earlier investigators[2,7,8,9,14,23] have used solubility in liquid SO_2 as a means of measuring the amount of extractable material and have described several types of equipment, in this investigation an entirely new apparatus has been designed and developed for a rapid, easily manipulated and inexpensive method for the extraction of liquid materials with SO_2. The extraction operation is carried on in an apparatus shown in its latest stage of development in longitudinal section in Figure 1 and in the photograph of Figure 2. The process consists in bubbling SO_2 into the material to be extracted which is cooled in a burette to —20°C. The SO_2 condenses and settles to the bottom of the burette with the extracted material and forms a layer which is separated from the oily layer above by a distinct line of demarcation and may be measured and drawn off readily. Subsequent extractions of the residual material are made in a similar manner.

The apparatus is enclosed in two concentric pyrex glass tubes held together with rubber stoppers at the ends. The tubes are 22 inches long and 2 and 2½ inches in diameter. The inner tube forms a reservoir for the cooling mixture and carries a 100 cc. burette which is held at the bottom by a rubber stopper and supported at the top by a clamp. The outer tube forms a dead air space and provides satisfactory insulation. The entire apparatus is supported by a heavy stand and clamps. The burette is graduated in .2 cc. divisions starting with zero at the bottom.

The cooling is done by direct expansion of liquid CO_2 into the cooling medium which is chloroform. A tank of carbon dioxide is placed in an inverted position in a suitable stand and is connected by quarter-inch copper tubing to a specially constructed expansion valve which is held rigid in the base of the apparatus by a clamp, as shown in Figure 1. This allows the carbon dioxide to expand inside the apparatus and at the same time permits the flow to be readily controlled in order to give the desired amount of cooling.

A calcium chloride drier is placed in

*This paper forms part of a dissertation submitted by Mr. Ward as partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Michigan.

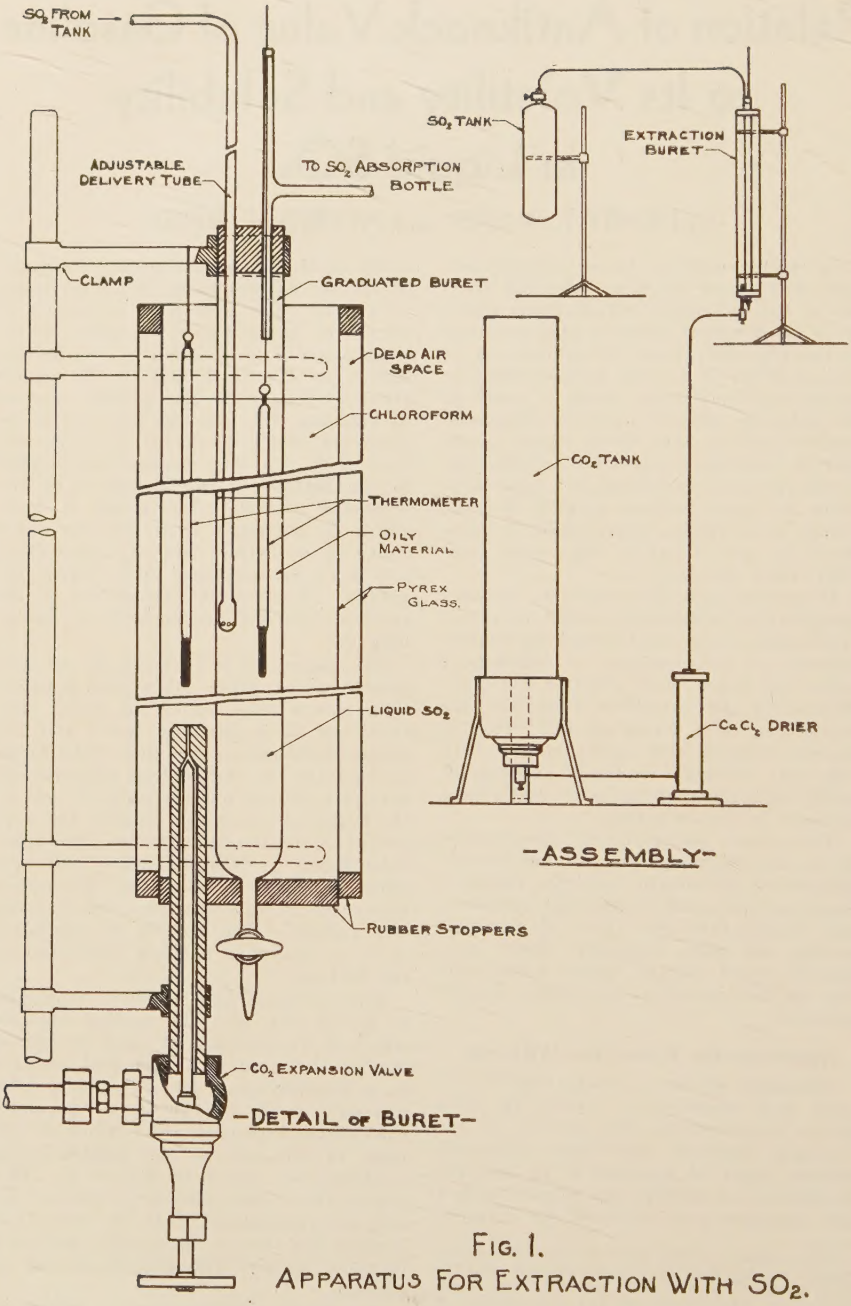

FIG. 1.
APPARATUS FOR EXTRACTION WITH SO_2.

the line from the tank to the valve in order to remove traces of moisture which are always present in the gas. The moisture would freeze and clog the needle valve and prevent steady operation if not removed. The drier is made of a piece of two-inch heavy iron pipe, twelve inches long, with caps and suitable fittings for the copper tube connections. All connections are welded since the drier must withstand the pressure of a full tank of carbon dioxide. A cap on the top for filling carries a lead washer.

The expansion valve is made from a standard eighth-inch brass elbow needle valve by drilling out the valve seat and placing in the vertical opening a brass tube four inches long and three-eighths inch outside diameter. The bore of the tube is three-sixteenths of an inch in diameter from the inlet end to within one-half inch of the other end, and from that point is one sixty-fourth of an inch in diameter. A piece of one-eighth inch steel bar stock is pointed at one end to form a needle, cut to the required length and mounted on the end of the valve stem to form the remainder of the valve. The stem is then seated in the brass tube by grinding. Finally the brass tube is brazed into position and the stem screwed down. The SO_2 delivery tube into the top of the burette is adjustable in length so that intimate contact between the SO_2 and the material being extracted can be made by raising and lowering the tube.

The temperatures are recorded on two thermometers, one hanging in the cooling medium and the other suspended in the burette so that the bulb is in the liquid.

Procedure for Extraction

The procedure for making an extraction is as follows: Fifty cubic centimeters of the material to be tested is measured into the burette from a pipette and then cooled to about —20°C. by adjustment of the CO_2 stream. Gaseous SO_2 is then conducted into the burette and at the same time the delivery tube is slowly raised and lowered to insure a thorough contact between the SO_2 and the liquid phase. The SO_2 is run in slowly enough so that the temperature is maintained always —12°C. which is the boiling point of the liquid. The volume of the oily material increases at first, while still remaining homogeneous. After its volume has increased by from 5 to 20 cc. the oily material suddenly becomes turbid and liquid SO_2 rapidly settles to the bottom of the burette. On initial introduction of SO_2 the color of the oily layer changes from colorless to various shades of yellow and sometimes to a deep red, the intensity increasing with the percentage extraction. When the SO_2 layer separates it retains the coloring matter, leaving the oily layer light yellow[5].

Sulphur dioxide is passed in until about 25 to 35 cc. of liquid have collected in the bottom of the burette. This layer is measured and then drawn off. The solvent is permitted to evaporate, either by allowing it to evaporate in the open air or by conducting it to the delivery tube for re-use for the next extraction. This operation is called the first extraction and the process is then repeated two times, collecting 25-30 cc. of liquid in the second extraction and 20-25 cc. in the third, either using fresh SO_2 from the tank or re-using SO_2 as mentioned above. The return of extracted vapors back into the burette by this procedure is probably not objectionable because the vapor pressure and therefore the quantity of extracted materials is low at the temperature of boiling SO_2. The amount of the increase in volume of the clear oily liquid, when SO_2 is first passed in, is a preliminary indication of the quantity of the final extraction.

After three extractions have been made, the unextracted material is drawn off into a specially constructed burette containing a 15 per cent solution of NaOH and shaken to neutralize the dissolved SO_2. This burette is an ordinary 50 cc. type with an enlarged reservoir of approximately 150 cc. capacity inserted between the stop-cock and graduations. After the shaking, water is run into the burette which causes the unextracted residue to rise into the graduated section, where its volume can be readily measured. The difference between the original volume (50 cc.) and the neutralized residue multiplied by two, gives directly the percentage extracted by SO_2.

Experimental Data

The chief materials which have been investigated and are reported here consist of a single type naphtha prepared by straight fractional distillation of Pennsylvania crude petroleum, and products prepared by fractional oxidation and vapor phase cracking of this naphtha. Twenty-eight commercial gasolines were

also tested. The boiling range of the naphtha is shown by the following data from the A.S.T.M. distillation: First Drop, 228°F.; 10 per cent, 312°F.; 90 per cent, 378°F.; Dry Point 418°F. This naphtha is referred to as untreated material.

The fractional oxidation of the naphtha was done by air without any catalyst in an electrically heated furnace. Various kinds of materials were used in making the furnace tubes for these operations. Horizontal furnaces were made with reatcion tubes seven-eighths inches in diameter made of quartz, porcelain, Enduro steel, and ordinary iron pipe. A vertical furnace with a 2-inch chrome nickel steel (KA2) tube was used in making the last thirty-seven thermal oxidation treatments. This portion of the work has been de-

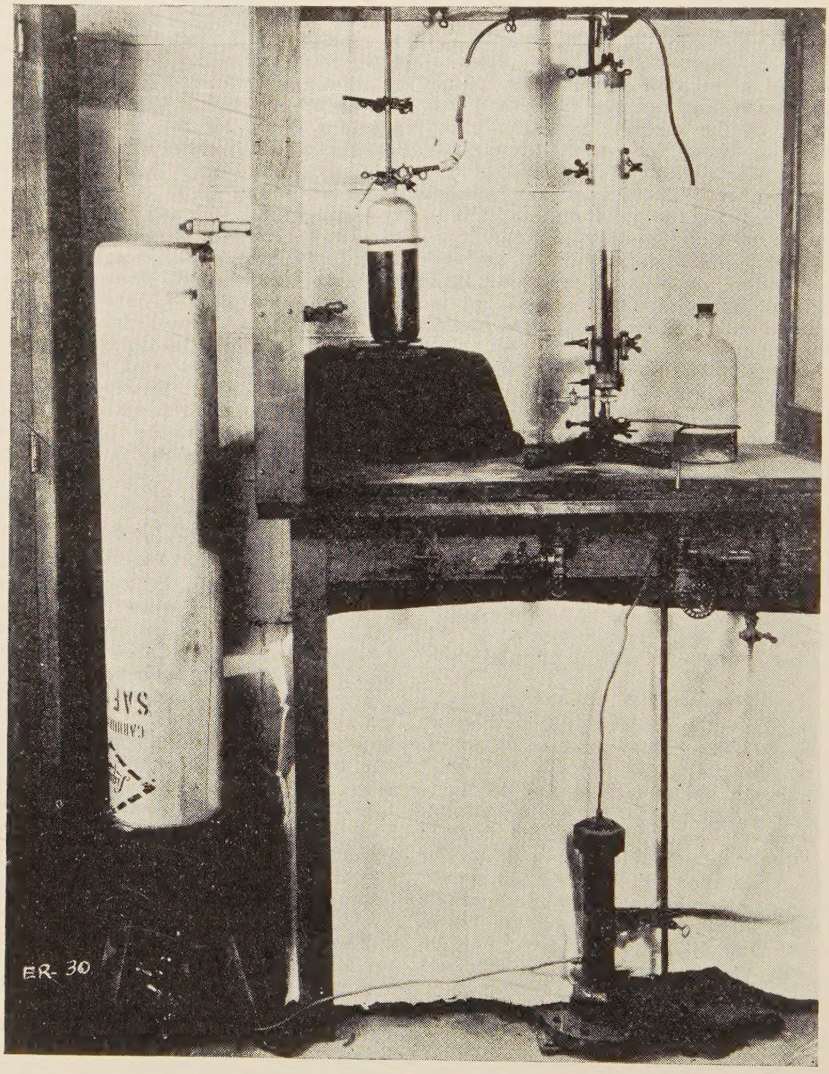

Figure 2—General view of apparatus used for extracting with SO_2

scribed elsewhere[a] and is briefly summarized here.

The hydrocarbon vapors and air were introduced into the heated tube and the products passed through water cooled condensers and the uncondensed gases were measured and analyzed. The oxidation reaction was silent and exothermic and very little heat was required from the outside after the reaction had started. The reaction was carried on at atmospheric pressure and at temperatures from 400 to 710°C (752-1,310°F.). The liquid product consisted of two layers, one oily, the other aqueous and distinctly acidic. The layers were separated and the oily material was washed with caustic or sodium carbonate solution and then distilled to a given endpoint. This purified product was used in the tests for knock rating and analysis, although in some cases the raw product was also examined. The treated product ranged from light yellow to orange in color and had a pungent odor. The cracked products were made in the same apparatus and in the same manner as the fractionally oxidized material, but without the use of air. The liquid product and uncondensed gases were handled as previously described. This product was similar in color to the other but possessed more of an odor of pressure distillate from cracking units.

In addition to the extraction with liquid SO_2 all the materials used were subjected to several other tests. The specific gravity of the naphtha was approximately 0.760 and of the oxidized material from 0.775 to 0.780. The cracked products showed slight increase in specific gravity over the original material. Titration with iodine showed an increasing absorption of I_2 with increase in the operating temperature of the furnace for producing the modified fuels. The amount of I_2 reduced was a measure of the total amount of reducing agents in the product but did not differentiate between olefinic hydrocarbons and oxidized products, such as aldehydes and ketones. An attempt was made to measure the amount of peroxides which might have been formed, by adding standard potassium iodide to the products and then titrating to determine the liberated iodine. The iodine first liberated by any oxidizing agents present, would in turn react with aldehydes and unsaturated hydrocarbons and unless the equivalent amount of oxidizing agents, such as peroxides was greater than the reducing agents, no value for iodine liberated could be reported.

Tests of the antiknock value of the various products were made in the Universal Test Engine of the Department of Engineering Research under the direction of Dr. G. G. Brown[b].

The details of the extraction method are illustrated in Table 1. This is the record of an oxidized naphtha sample which showed 44.6 per cent extracted by SO_2. The amount of liquid SO_2 to be used in each extraction and the number of extractions were decided as the result of experimental work in which several different variations were tested. Comparative tests of four and six extractions at —40°C were made and it was found that an average of only 1.5 cc more of the oily material were extracted in six extractions than in four extractions, or when 40 cc. additional liquid SO_2 had been used. Six extractions were therefore unnecessary, and later work indicated that three were adequate for comparative purposes. In the nineteen samples tested as mentioned above the total volumes of the SO_2 layers after four extractions were approximately 80 to 85 cc. No data were obtained at —20°C. which would permit a comparison of results of four and six extractions.

A comparison of the results of extractions at —40° and 20° C. substantiates the evidence published by Seyer and others [18, 19, 20, 21, 22] that the readily soluble materials decrease in solubility as the temperature of the extraction is lowered.

Discussion

The materials studied have been grouped according to their origin and volatility. The oxidized Pennsylvania naphthas form Groups A and B. Closely cut fractions of this same naphtha and their oxidized products form Groups C and D. The cracked naphthas form Group E and the commercial gasolines form Group F. Separate consideration has been given to seven samples oxidized at temperatures below 500°C. where there is evidence of interference due to peroxides.

The trend of knock rating with volatility has been studied by Geniesse and Huf[10] and by Brown[3]. It is shown from

[a] Schultz and White, Ind. and Eng. Chem. 24,1277 (1932).

[b] Brown and Zuck, The Oil and Gas Journal, 28, 44 (1930).

the experimental data recorded in the present paper that, for the gasolines used, a much more pronounced trend is revealed when both volatility and solubility in sulphur dioxide are considered.

In the four tables which follow, Tables 2 to 5, the results of the SO_2 extractions, knock ratings, and the 10 and 50 per cent points on the A.S.T.M. distillations of the manufactured products and commercial gasolines have been summarized. Only those oxidized naphthas on which the oxidation temperature was above 500° C (932°F) and whose knock ratings were determined within two or three days after the oxidation treatment have been included in these tables. Products obtained at temperatures below 500° C. have been placed in Table 6. The reasons for this separation will be discussed later.

Group A in Table 2 contains the data for those oxidized naphthas having the lowest volatility. The 10 per cent point on the A.S.T.M. distillation is from 276 to 296°F. and the 50 per cent point from 310 to 330°F. In Figure 3, curve A shows graphically the increase in octane number with increase in the per cent extracted by SO_2.

Table 2 also contains the data for those oxidized samples which have a 10 per cent point on the A.S.T.M. distillation of about 260°F. and a 50 per cent point about 310°F. and form Group B. The values for the octane numbers and the per cent extracted by SO_2 for this group are plotted as Curve B in Figure 3. The solubility in SO_2 of the members of this group is higher than that of the other groups and the curve has a lower slope. Moore[14] has shown that paraffins dissolve in the solution of olefine and

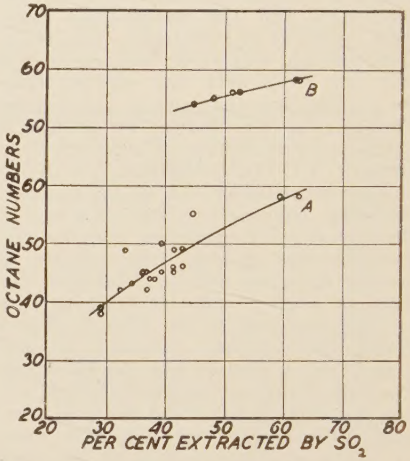

Figure 3.—Oxidized naphthas. Octane numbers vs. per cent extracted by SO_2. A—Group A. B—Group B.

SO_2 and the displacement of the curve is probably due to this effect.

Group E includes the Pennsylvania naphthas which had no treatment at all and also those which had been subjected to cracking and not oxidation. The data for both groups are given in Table 4 and shown graphically in Figure 4. The

TABLE 1—DATA RECORDED DURING THE EXTRACTION OF AN OXIDIZED NAPHTHA WITH SO_2 AT —20° C.

Run No. 297

Conditions—	Time	Temp. of $CHCl_3$ °C.	Temp. in Burette °C.	Total Volume cc.	Volume of SO_2 Layer cc.	Volume Oily Layer cc.
Room temp.	2:05	+23	+23	50.0	0	50.0
Cooled	2:15	—22	—20	47.7	0	47.7
SO_2 started:						
Became turbid	2:20	—25	—15	66.0	0	66.0
SO_2 stopped	2:25	—30	—16	...	30.0	...
Settling	2:28	—25	—23	...	33.2	...
Draw off	....	....	....	...	...	...
SO_2 started	2:31	—21	—20	39.9	0.3	39.6
SO_2 stopped	2:38	—21	—14	...	25.0	...
Settling	2:40	—20	—18	...	26.6	...
Draw off	....	....	....	...	...	...
SO_2 started	2:42	—17	—17	32.4	0.3	32.1
SO_2 stopped	2:49	—21	—18	...	21.0	...
Settling	2:52	—19	—17	. .	21.2	...
Draw off	....	....	....	...	...	...
Final	2:53	—18	—17	29.3	0.2	29.1

Volume of oily layer after neutralization with 15% NaOH solution = 27.7 cc.
Percentage extraction: 2 (50.0 — 27.7) = 44.6%.

octane numbers of the thermally treated naphthas are appreciably higher than those of the oxidized naphthas as represented in the curves of Figure 3. As an illustration, an extraction of 35 per cent shows an octane number of 54 for Group E and 43 for Group A.

The Pennsylvania naphthas and their modified products used in these tests having shown higher octane numbers for higher SO_2 solubility both in the original condition and in the oxidized and cracked forms, it became of interest to know how far separate fractions of the naphtha would also show this trend. About 50 gallons of the naphtha were redistilled in a column still and cut into six fractions. Each of these fractions was tested for SO_2 solubility and knock rating, and then subjected to oxidation and retested with results given in Group C of Table 3.

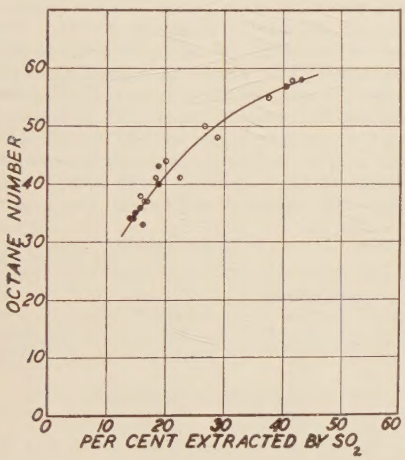

Fig. 4.—Untreated and cracked naphthas. Octane numbers vs. per cent extracted by SO_2 Group E. Untreated naphthas. O—Naphthas after vapor phase cracking

The original naphtha showed an SO_2 solubility of 16.2 and an octane number of 33. The octane numbers of the fractions varied from 54 to 10, the most volatile having the highest octane number (54) and the highest SO_2 solubility (19.6), and the least volatile the lowest octane number (10) and the lowest solubility (10.0). The intermediate fractions did not vary regularly, confirming the work of other investigators. The results of fractional oxidation of these separate fractions are shown in Group D of Table 3, and the values vary irregularly as they did in the original fractions. The SO_2 solubility does not show the trend of the octane numbers of these narrow fractions.

This investigation of Pennsylvania naphthas and the products formed from them by fractional oxidation or cracking having shown a correspondence between the SO_2 extraction and the knock rating provided the material did not have too narrow a range in boiling point, the method was then extended to commercial gasolines, Group F, of known knock rating which were supplied by Prof. G. G. Brown and tested in the usual manner with SO_2. The source of the

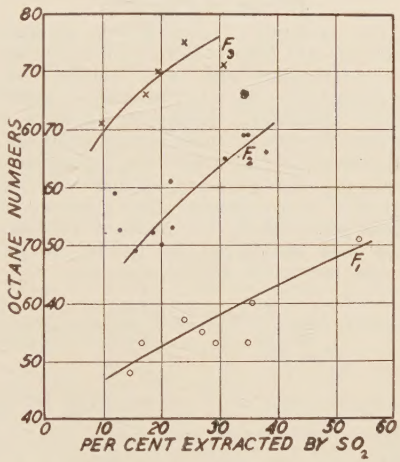

Fig. 5.—Commercial gasolines. Octane numbers vs. per cent extracted by SO_2. Group F. F_1—Group F_1. F_2—Group F_2. F_3—Group F_3.

crudes and the method of treatment in the refinery for the manufacture of these gasolines is not known.

The volatility of these samples is much higher than that of the modified naphthas. The samples have been divided into three groups, F_1, F_2, and F_3, according to volatility and a curve has been drawn for each group. The summary of the data of these samples is given in Table 5 and shown graphically in Figure 5. Group F_3 which is the most volatile group has a 10 per cent point on the A.S.T.M. distillation of about 125°F. Groups F_2 and F_1 have 10 per cent points of ap-

proximately 150 and 175°F. respectively. Five samples, 522, 532, 523, 433, and 409 have a 10 per cent point on the A.S.T.M. distillation above 200°F. The first two fall near the curve for the most volatile group and the others near the curve for the middle group. Exceptional variations in chemical composition[6,12,13,15,16] such as the presence of unidentified isomers, may be an explanation of these apparent discrepancies.

These commercial gasolines of unknown origin do not give an entirely satisfactory correlation between knock rating and solubility in liquid SO_2, but there is a definite trend toward higher solubility with increased octane number in each except the least volatile group.

Effects of Peroxides

The presence of peroxides in oxidized products has been indicated by a number of investigators who have oxidized pure hydrocarbons at temperatures below 500°C (932°F). Brunner[4] indicates a mechanism for the formation of peroxides. Moureau and Dufraisse[17] and others have indicated the presence of peroxides in oxidized hydrocarbons. The presence of these peroxides in the oxidized products has been considered by Lewis[11] to decrease the knock rating seriously.

All of the oxidized naphthas which have been previously discussed were produced at temperatures above 500° C. (932° F.). Those produced at 500° C. and below will be discussed here. Table 6 has been prepared to assist in the discussion of these samples. The first two samples which were oxidized at 300 and 400°C (572 and 752°F) respectively, averaged 19.0 cc. of n/10 Iodine evolved when a 10 cc. sample was shaken with KI solution. This is an evidence of the presence of peroxides. The last four samples were made with a furnace temperature of 500/C (932°F), and no iodine was liberated when these samples were tested. This does not mean that no peroxides were present because, as mentioned earlier, iodine liberated would be absorbed by unsaturated compounds and only surplus iodine would be shown by this test. It does indicate, however, that less peroxides were present in the product formed at 500°C. than at 400°C. The octane numbers of all of these samples are lower than would have been expected from the SO_2 solubilities reported in the earlier part of this paper. It is believed that at temperatures of 500°C (932°F) and below, sufficient peroxides remained in the finished product, even after washing with caustic, to depress the octane

TABLE 2—SUMMARY OF DATA ON OXIDIZED NAPHTHAS

Group A—10 per cent on A.S.T.M. distillatino ..... 276° to 296° F.
50 per cent on A.S.T.M. distillation ..... 310° to 330° F.

Run No.—	A.S.T.M. distillation 10% °F.	A.S.T.M. distillation 50% °F.	Approximate total volume of SO_2 layers cc.	Per cent extracted by SO_2 at —20° C.	Octane number
282	291	316	76	29.0	38
283	294	313	75	29.0	39
292	284	314	75	32.0	42
278	296	322	75	36.8	42
289	286	314	75	34.0	43
279	290	320	75	37.2	44
287	290	311	76	38.0	44
289A	284	312	76	35.8	45
276	284	320	75	36.0	45
290	282	314	76	37.0	45
312	287	331	75	39.2	45
281	284	314	75	41.2	45
312x	290	331	76	41.2	46
284	278	311	76	42.8	46
313	292	330	78	33.0	49
294	276	315	76	41.2	49
300	290	315	76	42.6	49
315	284	329	77	39.4	50
298	280	316	76	44.4	55
316	283	325	82	59.4	58
316	283	325	101	62.4	58
Group B—10 per cent on A.S.T.M. distillation					approx. 260° F.
50 per cent on A.S.T.M. distillation					approx. 310° F.
297	270	314	80	44.6	54
286	270	309	78	48.0	55
285	266	309	74	51.0	56
291	266	310	78	52.2	56
288	258	308	78	62.0	58
288	258	308	78	61.8	58

values and prevent any consistent relationship from appearing between the SO_2 solubilities and the octane values.

Ageing of Oxidized Naphthas

The previous discussion has included only those samples of oxidized naphthas on which the engine test was made within two or three days after the oxidation. Tests on Runs 294, 297 and 298 showed fair agreement between the knock ratings determined in two laboratories, but tests on runs with numbers above 300 showed depreciation in transit in tin containers. An examination of a sample of Run 298 which had been stored in a similar container in Ann Arbor showed a decrease from 55 to 44 octane number after two months' storage. The percentage extraction by SO_2 had changed in the same time from 44.4 to 42.8.

This product, as well as a number of others subsequently examined, became acidic in two weeks or more even though they had been initially purified by a caustic or soda wash and then stored in glass containers. Sample 261 was prepared by washing the product from 260 with dilute sodium hydroxide solution two weeks after the oxidation treatment. It was then given another engine test which showed the octane number had dropped from 44 to 37. The oxidizing effect of dissolved or loosely connected oxygen on the aldehydes may have been the cause of the acidity and decrease in knock rating. Bowen and Tietz[1] have shown that an acid and a peroxide were formed from acetaldehyde in the presence of oxygen and ultra-violet radiation.

Summary of Results

1. A dependable and relatively simple and inexpensive method for measuring the amount of material extractable from petroleum products with liquid SO_2 has been developed and described.

2. The results of extractions made on Pennsylvania naphthas before and after modification by vapor phase cracking and by partial oxidation have been compared with the knock ratings and volatility of these products. A consistent trend toward higher solubility in SO_2 with higher octane number has been clearly shown. This trend does not appear consistently when closely cut fractions of these naphthas are tested separately.

3. Experiments on motor fuels of unknown origin have indicated a similar trend between octane number, volatility, and solubility in SO_2, but the results are less consistent.

Bibliography

[1]Bowen and Tietz. J. Chem. Soc. 234 (1930).

[2]Bowrey. J. Inst. Pet. Tech. 3-4, 287, (1916-1918).

[3]Brown, G. G., Univ. of Mich, Engineering Research Bulletins No. 7 and No. 14.

[4]Brunner, Helv. Chim. Acta 13, 197 (1930).

[5]Canneri, G. Giorn. Chim. Ind. Applicata. 10, 73-76 (1929).

[6]Charch, Mack, and Boord. Ind. and Eng. Chem., 18, 334 (1926).

[7]Edeleanu. Z. Angew. Chem., 27, I 272 (1914).

[8]Edeleanu, Z. Angew. Chem., 36, 573 (1923).

[9]Engler and Ubbelohde. Z. Angew. Chem., 26, 177 (1913).

[10]Geniesse and Huf. Ind. and Eng. Chem., 20, 794 (1928).

[11]Lewis. J. Chem. Soc., 1555 (1927).

[12]Lovell, Campbell and Boyd. Ind. and Eng. Chem., 23, 26 (1931).

[13]Lovell, Campbell and Boyd. Ind. and Eng. Chem., 23, 555 (1931).

[14]Moore, Morrell and Egloff. Chem. and Met. Eng., 18, 8, 396 (1918).

[15]Morell and Egloff. Ind. and Eng. Chem., 18, 156 (1927).

[16]Morell and Egloff. Oil and Gas Jour., 25, No. 36, 156 (1927).

TABLE 3—PROPERTIES OF INDIVIDUAL NAPHTHA FRACTIONS—(GROUP C)

Sample—	A.S.T.M. distillation— 10% °F.	50% °F.	Per cent extracted by SO_2 at —20° C.	Octane number
Drum E_1	256	266	19 6	54
Drum E_2	285	289	13.6	29
Drum E_3	306	310	19.0	38
Drum E_4	324	326	17.2	30
Drum E_5	340	342	11.4	24
Drum E_6	370	378	10 0	10
Drum E	300	316	16 2	33
Group D—Oxidized Products from Individual Naphtha Fractions				
302	256	271	33.4	55
303	254	272	48 0	54
304	274	294	39.4	48
305	289	311	46.4	54
306	296	328	48.8	52
307	296	340	41.4	50
308	308	367	42 4	49
309	285	312	47.0	57
309	285	312	46.0	57
309	285	312	46 6	57

[17]Moreau and Defraisse. Chem. and Ind. 47, 819 (1928).
[18]Seyer and Dunbar. Trans. Roy. Soc. Can., 16, 307-10 (1922).
[19]Seyer and Gallaugher. Trans. Roy. Soc. Can., 20, 343-5 (1926).
[20]Seyer and Gill. Trans. Roy. Soc. Can., 18, 209-11 (1924).
[21]Seyer and Huggett. Trans. Roy. Soc. Can., 18, 213-16 (1924).
[22]Seyer and Todd. Ind. and Eng. Chem., 23, 325 (1931).
[23]Zerner, et al. Z. Angew. Chem., 35, 253 (1922).

TABLE 4—SUMMARY OF DATA ON UNTREATED AND CRACKED NAPHTHAS (GROUP E)

Sample—	A.S.T.M. distillation 10% °F.	A.S.T.M. distillation 50% °F.	Per cent extracted by SO_2 at —20° C.	Octane number
Cracked Naphthas				
262	312	328	15.6	36
274	314	327	16.4	37
277	306	320	16.6	37
275	313	327	15.6	38
299	294	314	18.8	40
271	307	327	18 4	41
293	278	312	22 4	41
270	312	328	20.0	44
310	274	326	28.8	48
295	274	311	26 6	50
311	268	326	37.2	55
314	250	320	40.4	57
296	270	320	43.0	58
296	270	320	41.2	58
Untreated Naphthas				
Drum F	312	335	14.6	34
Drum E	300	316	16.2	33
Drum D	309	322	14.8	35
Drum C	312	328	14 0	34
Drum B	196	276	18.6	43

TABLE 5—SUMMARY OF DATA ON COMMERCIAL GASOLINES (GROUP F)

Sample—	A.S.T.M. distillation 10% °F.	A.S.T.M. distillation 50% °F.	Per cent extracted by SO_2 at —20° C.	Octane number
515	135	280	10.0	61
440	102	147	17.6	66
516	127	276	19.6	70
392	122	271	30.8	71
514	120	259	24.0	75
502	157	255	15.6	49
519	151	265	20.2	50
531	161	270	18.6	52
3R	160	273	22.9	53
434	150	274	13.0	53
432	156	255	11.8	59
431	146	261	21.6	61
539	145	266	30.8	65
422	151	241	38.0	66
511	144	269	35.0	69
511	144	269	34.4	69
404	166	254	14.6	48
513	180	257	16.6	53
437	171	282	29.4	53
436	173	283	34.6	53
438	173	279	27.0	55
439	169	280	24.0	57
435	171	279	35.6	60
507	177	275	54.0	71
433	207	308	12.4	50
523	234	321	14.2	54
532	231	314	34.8	79
522	231	314	31.6	80
409	201	324	54.2	86

TABLE 6—OXIDIZED NAPHTHAS PRODUCED AT 500° C. OR BELOW

Run No. →	Furnace temp. °C.	Iodine liberated cc. N/10 I_2	Per cent extracted by SO_2 At —40° C	Per cent extracted by SO_2 At —20° C.	Octane number
242	300	19.6	34.4	....	41
243	400	18.5	32.6	....	40
280	410	(*)	....	48.2	47
244	500	....	32.4	....	44
252	500	....	28.0	....	43
255	500	....	30.2	....	41
260	500	....	26.4	....	44

*Not tested.